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Kraków, 09-09-2025

Review of the doctoral dissertation of Martyna Mańka, M.Sc.

The doctoral dissertation of Ms Martyna Mańka, entitled *"Amino-functionalized MOF based thin films as sensory platforms for detection of aldehydes"* was prepared within a cotutelle framework between the Faculty of Chemistry, Adam Mickiewicz University in Poznań (at the Department of Coordination and Supramolecular Chemistry, under the supervision of Prof. Violetta Patroniak) and the Institut de Science et d'Ingénierie Supramoléculaires, Université de Strasbourg (with the scientific mentorship of Dr Artur Ciesielski). The project was supported by the France Excellence Scholarship and the Polish "Initiative of Excellence – Research University" program, which provided the candidate with demanding opportunity to carry out research in two leading laboratories.

At the outset, I would like to emphasize that my own experience with metal–organic frameworks (MOFs) has been largely shaped by their biomedical and photocatalytic applications, rather than the most recent strategies of their rational design and controlled functionalization as electrochemical sensors. Approaching Ms Mańka's dissertation from this perspective proved particularly instructive and I have therefore read the manuscript with close attention, both to the conceptual architecture and to the quality and consistency of the experimental work. MOFs, as crystalline porous architectures built from metal clusters and multitopic ligands, are widely recognized for their designability (the possibility of tailoring properties by rational selection of building blocks and synthetic conditions). Their potential uses, ranging from adsorption and catalysis to energy storage, medicine and sensing, are offset by persistent challenges, such as limited structural robustness under realistic conditions, compatibility of components, and precise control over structure–function relationships at the molecular scale. These issues form a demanding and highly relevant backdrop for the dissertation under review. A further distinguishing feature of Ms Mańka's doctoral path is the double-degree program (cotutelle) itself. This competitive and logistically complex framework provided the candidate with complementary training, access to diverse methodological approaches, and the opportunity to acquire experience with advanced instrumentation in both

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Poznań and Strasbourg. It is worth stressing that such arrangements are far from routine, and the successful completion of this program attests to the candidate's determination, adaptability and intellectual independence. While the overall publication record is less extensive than in some single-track doctorates, the thesis itself shows a high degree of scrupulousness in experimentation, careful data treatment and critical analysis- all qualities that deserve recognition at the doctoral level.

The dissertation comprises slightly more than 180 pages and is organized in a clear, conventional manner. Following the title pages, acknowledgments and a trilingual abstract (English, French, Polish), it begins with an Introduction and a section defining the research aims. The core of the work consists of two main parts: Experimental techniques and methods, and Results and discussion. The thesis concludes with a concise Summary and outlook, an extensive reference list of 403 entries complemented by shorter bibliographies after each chapter, and appendices including a statement of contributions, curriculum vitae, and a record of scientific achievements, notably one publication in *Chemical Communications* and earlier work in *Biomolecules* not directly incorporated into the thesis.

The Introduction presents the general concept of metal–organic frameworks, outlining their structural principles, porosity, and modularity, as well as their functional potential with particular focus on sensing applications. The candidate explains how properties of MOFs can be tuned by rational choice of metal ions and organic linkers, emphasizing amino-functionalization as a strategy to enhance reactivity and enable specific interactions with aldehydes. This framing provides a clear rationale for the sensing studies developed in the thesis. At the same time, the introductory part remains relatively concise compared with the vast literature in the field. Recent methodological advances, such as defect engineering, mixed-linker strategies, post-synthetic modifications, or integration of MOFs with polymers, covalent organic frameworks and nanostructured oxides, are mentioned only briefly, and achievements in MOF-based sensors are presented in outline, without a critical discussion of how the present project positions itself against state-of-the-art approaches. As a result, the chapter establishes a functional background but could have benefited from a more synthetic perspective that better highlights the novelty of the work and clarifies the knowledge gaps it aims to address. From a presentation standpoint, the text is rather dense; although several schematic illustrations are

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included, additional visual elements would have enhanced readability and more effectively conveyed the design logic, particularly for readers less familiar with the field.

The aims of the dissertation are stated in a separate subsection. They are clear and well aligned with the main theme of the thesis: the design, fabrication and characterization of thin MOF films functionalized with amino groups, and the evaluation of these films as sensory platforms for aldehyde detection. The objectives are subdivided into (i) synthesis and structural characterization of amino-functionalized MOFs, (ii) preparation and optimization of thin films, (iii) physicochemical and morphological analysis, and (iv) testing of the sensing performance towards selected aldehydes. These goals are well defined and provide a logical structure for the subsequent chapters.

In summary, the introductory part of the dissertation successfully establishes the general framework of the research and states the objectives in a concise manner. However, it could be strengthened by a more comprehensive discussion of frontier directions in MOF design and by a richer use of graphical elements. The scientific rationale for focusing on aldehyde detection is clear, yet a deeper analysis of the broader context of MOF-based sensors (including their competition with polymer-based or nanostructured oxide platforms) would further underline the significance of the chosen research problem.

The Experimental section is well structured and divided into subsections covering chemical, structural and morphological characterization of the studied MOFs, together with electrochemical protocols used in sensing experiments. Detailed descriptions are provided for infrared spectroscopy, X-ray diffraction, XPS, thermogravimetric analysis, BET surface area measurements, and electron microscopy, consistently including references to specific instruments and collaborating laboratories. This level of detail ensures reproducibility and reflects good scientific practice. Particularly convincing is the use of XPS, not only for compositional verification but also to confirm imine bond formation upon aldehyde exposure, directly supporting the proposed sensing mechanism. Likewise, thermogravimetric analysis with clearly defined heating conditions and BET porosimetry with specified models demonstrate methodological care aligned with the aims of the work. At the same time, certain parts could be more concise and parameter-specific. The XRD description, for instance, tends to be didactic and somewhat repetitive, without fully addressing details critical for thin-film

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studies, while the SEM section adopts a textbook-like style rather than providing precise experimental conditions. Despite these minor shortcomings, the methods chapter convincingly demonstrates the candidate's ability to employ a broad range of modern techniques, and it provides a solid foundation for the scientific results presented later in the dissertation.

The Results and discussion chapters form the scientific core of the dissertation, presenting the systematic design, fabrication and assessment of thin MOF films functionalized with amino groups. The work is organized into sections on structural properties, morphology, pore size distribution, stability studies, and most importantly, the electrochemical sensing performance towards formaldehyde, acetaldehyde and benzaldehyde. Experimental data are complemented, where appropriate, by computational studies (DFT calculations performed in collaboration with the University of Warsaw). The presentation is generally clear, supported by spectra, microscopic images, and tables summarizing sensitivity, detection limits, linear ranges, and selectivity tests, which allow for a quantitative evaluation of sensor performance. Morphological and textural analyses are coherent: SEM images and BET surface area measurements confirm porosity, while TGA data demonstrate that the films maintain stability under sensing conditions. These characterizations, though sometimes presented in a rather descriptive style, convincingly support the claim that the candidate obtained stable and reproducible materials. A particularly valuable aspect is the correlation of XPS evidence, most notably signals of imine formation upon aldehyde exposure with electrochemical response, which provides mechanistic weight to the observed sensor activity. The electrochemical studies themselves constitute the most original contribution, showing that amino-functionalization enhances both selectivity and response, while the comparative evaluation of Co-, Cu- and Ni-based MOFs offers useful insight into the role of the central metal ion. Although the discussion could have gone further in critically assessing reproducibility and long-term stability, the chapters demonstrate the candidate's mastery of a wide range of experimental techniques and ability to integrate them into a coherent and relevant study. The findings are original, well aligned with the stated aims, and contribute to a deeper understanding of MOF-based sensing platforms.

In my opinion the novelty of the work lies not only in the preparation of such films, but also in the integration of mechanistic insight most notably, the use of XPS to confirm Schiff

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base formation during analyte exposure into the interpretation of sensor behavior. This combination of structural characterization with functional testing strengthens the credibility of the conclusions. Another valuable element is the inclusion of recovery tests on real samples, which, although limited in scope, point towards practical applicability. The research presented in the dissertation with no doubts addresses a problem of scientific relevance, it shows a consistent methodological approach, and it provides novel results that can serve as a platform for future development. In particular, the ability to link molecular-level functionalization with measurable device performance is an important step towards translating MOF chemistry into real sensing technologies.

Although the dissertation is carefully prepared, a few aspects deserve critical comment. The division of the bibliography into a very long list (over 400 entries) followed by a short lists of cited literature is unconventional and may confuse the reader; consolidation or clearer justification would improve editorial consistency. I also noted some terminological inaccuracies. In the list of symbols, the candidate uses “E” for molar absorptivity, which is non-standard and potentially misleading, since E is widely reserved for energy; the correct symbol is ε , and the accepted term is “molar absorption coefficient”. Furthermore, the thesis states that pKa is “the acid dissociated constant”, which is incorrect; the proper definition is “the negative logarithm of the acid dissociation constant”. Similarly, the abbreviation “ACS” is explained as “absorbance caused enhancement”, which is not standard usage and requires correction. These may appear as minor lapses, but they detract from the otherwise careful preparation of the manuscript.

Additionally, during the defense I would like to hear the PhD candidate’s views on:

- whether alternative functional groups or modification strategies were considered, and how her chosen approach compares with those used by other research groups (advantages and disadvantages),
- the main experimental difficulties or limitations encountered when applying desire functionalization of MOF-based materials,
- possible cases of MOFs instability (amorphization, loss of porosity, inconsistent results) and how these were recognized or mitigated,

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- the comparison between MOFs and zeolites in various applications, with particular attention to areas where each class of materials might hold an advantage.

In conclusion, the doctoral dissertation of Ms Martyna Mańka demonstrates originality, methodological rigor and interdisciplinary breadth. The candidate has convincingly shown the potential of amino-functionalized MOF thin films as sensory platforms for aldehyde detection, integrating careful structural characterization with functional testing. Despite minor shortcomings in terminology, presentation and consistency of experimental reporting, the thesis clearly fulfils the criteria of a doctoral dissertation in chemical sciences. Taking into account the scientific quality, the interdisciplinary scope and the editorial diligence of the work, I state with full conviction that the dissertation meets all requirements specified in Art. 187 of the Act of 20 July 2018 on Higher Education and Science (Journal of Laws 2020, item 85, as amended) and merits admission to public defense. I therefore formally request that Martyna Mańka, M.Sc., be admitted to the next stages of the doctoral procedure.

Yours sincerely,

Elektronicznie
podpisany przez
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